CHAPTER 2

EXPERIMENTAL METHODS

2.1 SYNTHESIS METHODOLOGIES

2.1.1 Chemicals

Hydrothermal synthesis of MeAPO-5 and MeAPO-11 was carried out using triethylamine (minimum 99% Sigma-Aldrich) and dipropylamine (99% Aldrich) as organic template. Aluminium oxide hydroxide (Catapal B Alumina, Sasol) and aluminium isopropoxide (98% Aldrich) were used as the source for aluminium whereas phosphoric acid (≥85 wt.% Sigma-Aldrich), vanadyl sulfate hydrate (97% Aldrich), titanium (IV) isopropoxide (97% Aldrich), iron (II) acetate (95% Aldrich) and cobalt (II) nitrate hexahydrate (98% Sigma-Aldrich) were used as the sources for phosphorus, vanadium, titanium, iron and cobalt respectively. These chemicals were used as such without further purification. Deionized water was used in all the synthesis procedures. Synthesis was carried out by following the procedure described in the literature (Flanigen et al 1988 and 1988a) and slightly modified according to Elangovan and Murugesan (1997).

2.1.2 Synthesis of AlPO-5

AlPO₄-5 was synthesized using the gel composition 1 TEA: 1 Al₂O₃:1 P₂O₅: 40 H₂O. A day prior to the synthesis, 28.37 g of aluminium isopropoxide was soaked in 30 ml distilled water. On the day of the synthesis, it was vigorously stirred for 2 h. Phosphoric acid (9.5 ml) diluted with 20 ml
water was added dropwise to the above mixture. The slurry was stirred for another 2 h and triethylamine (TEA) (9.7 ml) was added drop by drop. The gel was finally stirred for another 2 h. The pH of the gel was 4.5. The resultant gel was placed in a Teflon lined stainless steel autoclave under autogeneous pressure in static condition at 175° C for 24 h. Then the autoclave was cooled to room temperature to get the product whose pH was 9.4. The product was washed several times with water and dried in an air oven at 110° C for 12 h. Finally the products were calcined by heating until 400° C (heating rate 1° C/min) in a flow of nitrogen. After that, it was again heated upto 550° C with the same ramp speed in O₂ and kept at the same temperature for 12 h in a flow of oxygen.

2.1.3 Synthesis of CoAPO-5

The gel composition used in the synthesis was 0.1 CoO: 1 TEA: 1 Al₂O₃: 1 P₂O₅: 40 H₂O. Aluminium isopropoxide (28.37 g) was soaked in 30 ml distilled water in a Teflon lined stainless steel autoclave and kept aging for 24 h. The contents were vigorously stirred for 2 h. Cobalt nitrate (2.01 g) was dissolved in 9.5 ml phosphoric acid and 20 ml distilled water. The clear pink solution was added dropwise to the contents in the autoclave and stirred again for 2 h. Triethylamine (TEA) (9.7 ml) was added slowly and continued the stirring for another 2 h and the pH of the initial gel was 4.2. This was kept under autogeneous pressure at 175° C for 24 h. After cooling the autoclave, pH of the product was found to be 9.3. Solid product was washed several times with distilled water, filtered and dried in an air oven at 110° C for 12 h. Finally the product was calcined by heating until 400° C with (heating rate 1° C/min) a flow of nitrogen. After that, it was again heated upto 550° C with the same ramp speed in O₂ and kept at the same temperature for 12 h in a flow of oxygen.
2.1.4 Synthesis of CoAPO-11

CoAPO-11 was synthesized using the gel composition 0.08 CoO: 1 DPA: 0.95 Al₂O₃: 1 P₂O₅: 50 H₂O. Aluminium oxide hydroxide (7.92 g) was added to 37.5 ml distilled water in a polypropylene beaker. It was vigorously stirred for 2 h. Cobalt nitrate (1.38 g) dissolved in phosphoric acid (9.5 ml) and distilled water (25 ml) was added dropwise. This slurry was again stirred for 2 h and dipropylamine (DPA) (9.52 ml) was added drop by drop. The gel was finally stirred for another 2 h and pH of the gel was 3.8. Then the gel was transferred to a Teflon lined autoclave and kept at autogeneous pressure at 197º C for 24 h. After this, the autoclave was cooled to room temperature to get the product whose pH was 9.4. The solid product was washed several times with distilled water, filtered and dried in an air oven at 110º C for 12 h. Finally the product was calcined by heating until 500º C (heating rate 1º C/min) in a flow of nitrogen. After that, it was again heated upto 530º C with the same ramp speed in O₂ and kept at the same temperature for 12 h in a flow of oxygen.

2.1.5 Synthesis of VAPO-5

VAPO-5 was synthesized using the gel composition 0.1 V₂O₅: 1 TEA: 1 Al₂O₃: 1 P₂O₅: 40 H₂O. Aluminium isopropoxide (28.37 g) with water (30 ml) was aged for 24 h in a Teflon lined stainless steel autoclave and then stirred vigorously for 2 h. Vanadyl sulfate (2.26 g) was mixed with phosphoric acid (9.5 ml) and distilled water (20 ml). The blue coloured solution was added to the autoclave and stirred again for 2 h. Triethylamine (TEA) (9.7 ml) was added drop by drop and stirred for another 2 h. The pH before synthesis was measured as 4.2. This was kept under autogeneous pressure at 175º C for 24 h. After cooling the autoclave, the pH of the product was found to be 9.6. The solid product was washed several times with distilled water, filtered and dried at 110º C for 12 h. Finally the product was
calcined by heating until 400º C (heating rate 1º C/min) in a flow of nitrogen. After that, it was again heated upto 550º C with the same ramp speed in O₂ and kept at the same temperature for 12 h in a flow of oxygen.

2.1.6 Synthesis of VAPO-11

The gel composition used in the synthesis of VAPO-11 was 0.05 V₂O₅: 1 DPA: 0.95 Al₂O₃: 1 P₂O₅: 50 H₂O. Aluminium oxide hydroxide (7.92 g) was added to distilled water (37.5 ml) in a polypropylene beaker and stirred vigorously for 2 h. A mixture of 1.13 g vanadyl sulfate, 9.5 ml phosphoric acid and 25 ml distilled water was added slowly to the content in the beaker and again stirred for 2 h. Dipropylamine (DPA) (9.52 ml) was added and the stirring continued for another 2 h. The pH of the resultant gel was 3.2. The gel was then transferred to a Teflon lined stainless steel autoclave and kept at autogeneous pressure at 197º C for 24 h. After this, the autoclave was cooled to get the product whose pH was 9.7. The product was washed several times with distilled water, filtered and dried in an air oven at 110º C for 12 h. Finally the product was calcined by heating until 500º C (heating rate 1º C/min) in a flow of nitrogen. After that, it was again heated upto 530º C with the same ramp speed in O₂ and kept at the same temperature for 12 h in a flow of oxygen.

2.1.7 Synthesis of FeAPO-5

The gel composition used for FeAPO-5 synthesis was 0.1 Fe₂O₃: 1 TEA: 1 Al₂O₃: 1 P₂O₅: 40 H₂O. Aluminium oxide hydroxide (8.33 g) was added to distilled water (30 ml) in a polypropylene beaker and vigorously stirred for 2 h. While stirring iron acetate (2.41 g) dissolved in phosphoric acid (9.5 ml) and distilled water (20 ml) was added drop by drop and stirring continued for 2 h. Triethylamine (TEA) (9.7 ml) was added slowly and stirred for another 2 h. The pH of the gel was found to be 4.4. The gel was then
transferred to a Teflon lined stainless steel autoclave and kept at autogeneous pressure at 175º C for 24 h. After this, the autoclave was cooled to room temperature to get the product whose pH was 9.5. The product was washed several times with distilled water, filtered and dried in an air oven at 110º C for 12 h. Finally the product was calcined by heating until 400º C (heating rate 1º C/min) in a flow of nitrogen. After that, it was again heated upto 550º C with the same ramp speed in O₂ and kept at the same temperature for 12 h in a flow of oxygen.

2.1.8 Synthesis of TAPO-5

TAPO-5 was synthesized using the following gel composition 0.1 TiO₂: 1 TEA: 1 Al₂O₃: 1 P₂O₅: 40 H₂O. Aluminium oxide hydroxide (8.33 g) was added to distilled water (30 ml) in a polypropylene beaker and stirred vigorously for 2 h. Titanium isopropoxide (4.1 ml) mixed with phosphoric acid (9.5 ml) and distilled water (20 ml) was added drop by drop and again stirred for 2 h. Triethylamine (TEA) (9.7 ml) was added dropwise and stirred for another 2 h. The pH of the gel was found to be 3.9. Then the gel was transferred to a Teflon lined stainless steel autoclave and kept at autogeneous pressure at 175º C for 24 h. After this, the autoclave was cooled to room temperature to get the product whose pH was 9.7. The solid product was washed several times with distilled water, filtered and dried in an air oven at 110º C for 12 h. Finally the product was calcined by heating until 400º C (heating rate 1º C/min) in a flow of nitrogen. After that, it was again heated upto 550º C with the same ramp speed in O₂ and kept at the same temperature for 12 h in a flow of oxygen.
2.2 PHYSICO-CHEMICAL CHARACTERIZATION TECHNIQUES

2.2.1 X-Ray Diffraction (XRD)

Powder XRD patterns were obtained in the 2θ range of 5 – 50° by using a Philips PW1830 X-ray powder diffractometer with Ni filtered CuKα (λ = 1.5406 Å) source at 40 kV and 20 mA. A scintillation counter with 2θ scan speed of 2.0 min⁻¹ and with slits of 0.5°, 0.5° and 0.3 mm for scattering, divergence and receiving respectively at room temperature.

2.2.2 Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Analysis (EDX)

Morphological analysis was carried out by a Zeiss EVO50 Scanning Electron Microscope (SEM) equipped with a LaB₆ filament under an EHT of 15 kV with a working distance of 8.5 mm and a probe current of 10 pA. The instrument was connected to an Oxford Instruments INCA Energy 200 EDS equipped with an Oxford SATW pentafet Si(Li) detector. Analytical conditions for the quantification of the elements were the following: EHT = 15 kV, WD = 8.5 mm and PT = 5 µs. Typically, under these conditions, a count rate of 2kcps was obtained and spectra were recorded for a live time of 90 seconds.

2.2.3 Transmission Electron Microscope (TEM)

Observations of the powders by Transmission Electron Microscopy (TEM) were performed with a JEOL 3010-UHR with acceleration potential of 300 kV. Samples were dispersed on a copper grid covered with a lacey carbon film.
2.2.4 **Surface Area and Porosity Analysis**

Volumetric analysis were carried out by measuring nitrogen adsorption isotherms at liquid nitrogen temperature in the pressure range from 0 to 760 mm Hg using Micromeritics ASAP 2010 surface area and porosity analyzer. Prior to the adsorption, the calcined samples were outgassed for 1 h at 373 K, 1 h at 473 K and 1 h at 573 K and finally 4 h at 673 K under high vacuum (final pressure: 1.0x10^{-3} mm Hg). Specific surface area of the samples was determined by the Brunauer-Emmett-Teller equation using data collected in the range 0.07 to 0.25 as the value of maximum relative pressure.

2.2.5 **Resonant Raman Spectroscopy**

UV Raman spectra were recorded using a Renishaw micro-Raman System 1000 by exciting with a frequency doubled Ar⁺ laser, operating at 244 nm (40984 cm⁻¹). The photons scattered by the sample were dispersed by a 3600 lines/mm grating monochromator and simultaneously collected on a CCD camera. The collection optic was a 15X objective. A laser power < 5 mW on the sample was used. The spectra were recorded by collecting 50 acquisitions (each of 20 s) on a self-supporting wafer put in a home-made cell with a suprasil quartz cuvette that allowed measurements in a controlled atmosphere.

2.2.6 **Samples Treatment**

Prior to the DRS-UV-Vis and FT-IR studies, the samples connected to high vacuum line (in Figure 2.1) were oxidized with repeated cycles of O₂ (p ≥ 100 torr) at 823 K for 3 to 8 h and also reduced with the same pressure of H₂ at 673 K for 3 to 8 h. After the redox treatments samples were evacuated at the same temperature and cooled to room temperature (RT) for DRS-UV-Vis or FT-IR measurements. High purity O₂, H₂, NO, NH₃, CO and
Figure 2.1 High vacuum line for sample pretreatment
$^{13}$C labeled CO were supplied by PRAXAIR, Belgium. CD$_3$CN was supplied by Aldrich. Gases were passed through a liquid nitrogen trap before adsorption. A methanol/liquid nitrogen trap was employed for NO previously purified by distillation.

2.2.7 Fourier Transform Infrared (FT-IR) Spectroscopy

FT-IR measurements were recorded on a Bruker IFS 88 spectrometer equipped with mercury cadmium telluride (MCT) and deuterated triglycine sulfate (DTGS) detector, working with a resolution of 4 cm$^{-1}$. 64 scans were accumulated for each spectrum. The activation of the samples was directly carried out in the vacuum cells employed for the measurements. The detailed procedure is as follows:

Each sample was vigorously grinded and pressurized to obtain a thin pellet with superficial density between 3.0 and 9.0 mg/cm$^2$ using a hydraulic press working at ca 7.0 tons. The pellet was inserted in a gold envelope with $\geq$ 1.0 cm$^2$ opening in the center to protect it. It was then inserted into the vacuum quartz cell used for activation and measurement. Two different design quartz cells equipped with KBr windows were employed in controlled atmosphere (vacuum, redox atmosphere and gas dosage), which have different shape depending on the working temperature range (Figure 2.2 A and B). One is for room temperature (RT) measurements (Figure 2.2 A) and the other allows to reduce the temperature (110 K) on the pellet by filling an internal cavity with liquid nitrogen (Figure 2.2 B).

The cell containing the pre-activated sample was connected to a vacuum line (similar to the one shown in Figure 2.1) close to the FT-IR instrument to permit in situ gas dosages. The experiments were carried out at room temperature and also at liquid nitrogen temperature (LNT) (estimated temperature on the pellet ca. 110 K), performed by consecutive addition of
Figure 2.2 FT-IR cell (A) room temperature (RT) and (B) liquid nitrogen temperature (LNT)
liquid nitrogen in an adapted quartz cell (Figure 2.2 B). After increasing the pressure of probe molecule from the initial pressure of 0.005 – 1 mbar to final pressure of 20 – 100 torr, the samples were kept in contact with probe molecules at higher pressure for half an hour and finally the equilibrium pressure was reduced step by step to obtain a sequence of IR spectra corresponding to increasing coverage, time evolution and decreasing coverage. The sample spectrum collected before gas dosage was used as reference for obtaining the reported background-subtracted spectra. When necessary the reported IR spectra were normalized with respect to the pellet thickness. Probe molecules were passed through a liquid nitrogen trap before adsorption, a methanol/liquid nitrogen trap was employed for NO, previously purified by distillation.

2.2.8 DRS-UV-Vis Spectroscopy

DRS-UV-Vis measurements were performed on samples that were already calcined. All measurements were performed at room temperature (RT) on powdered samples using a Perkin-Elmer (Lambda 19) spectrometer equipped with an integrating sphere with BaSO$_4$ as reference. Spectra were recorded in 190 – 2500 nm range at a scan rate of 240 nm/min with a step size of 1 nm and slit opening of 4 mm. The measured intensities were converted with the Kubelka-Munk function. For these studies, a tubular cell with quartz window was employed, allowing thermal treatments in vacuo and in redox atmosphere, gas dosage and in situ measurements (Figure 2.3).

Figure 2.3 Tubular cell for DRS-UV-Vis measurement